

PCTFE BLOW MOLDING CONTAINERS

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BACKGROUND OF THE INVENTIONFIELD OF THE INVENTION

10 The invention relates to shaped articles including a layer of a fluoropolymer and a layer of a thermoplastic polymer. More particularly, the invention pertains to molded articles, particularly molded bottles, having a layer of a fluoropolymer attached to a layer of a polyethylene via an intermediate adhesive. The adhesives that are employed are useful in adhering layers of dissimilar polymeric materials that are otherwise incompatible and achieve a significantly improved interlayer
15 bond strength between a fluoropolymer layer and a thermoplastic polymer layer.

DESCRIPTION OF THE RELATED ART

20 A wide variety of thermoplastic polymers and bottle containers formed from such thermoplastic polymers are known. Important physical characteristics of such a container includes its barrier properties, including barriers to gas, aroma, and/or vapor such as water vapor, as well as its physical characteristics, such as toughness, clarity, wear and weathering resistances, light-transmittance and chemical inertness. These properties are especially important in packaging applications for food or medical products.

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It is well known in the art to produce multilayer fluoropolymer films. See, for example, U.S. patents 4,146,521; 4,659,625; 4,677,017; 5,139,878; 5,855,977; 6,096,428; 6,138,830; and 6,197,393 . Many fluoropolymer materials are

commonly known for their excellent moisture and vapor barrier properties, as well as their chemical resistance, and therefore are desirable components of packaging articles, particularly lidding films, blister packages and bottle containers. In addition, fluoropolymers exhibit high thermal stability and excellent toughness. However, such use of fluoropolymers is restricted to specialty packaging applications due to their relatively high cost. A suitable means of reducing the cost of a packaging material fabricated from a costly polymer is to form multilayer structures in which the polymer is laminated with other, less costly polymer layers. This approach is particularly desirable for the fluoropolymer packaging applications since a thin layer of the fluoropolymer is often all that is needed to take advantage of the desirable properties of the fluoropolymer while minimizing the cost. However, fluoropolymers do not adhere strongly to most other polymers. In fact, most fluoropolymers are known for their non-stick characteristics. This is very disadvantageous, because poor bond strength between layers can result in the delamination of multilayer structures.

To improve the bond strength between a layer of a fluoropolymer and a layer of a thermoplastic polymer (e.g. a non-fluoropolymer layer), an adhesive tie layer may be used between adjacent layers. For example, U.S. patent 4,677,017 discloses coextruded multilayer films which include at least one fluoropolymer film and at least one thermoplastic film which are joined by the use of an adhesive polymer, particularly ethylene/vinyl acetate polymers, as an adhesive tie layer. U.S. patent 4,659,625 discloses a fluoropolymer multilayer film structure which utilizes a vinyl acetate polymer adhesive tie layer. U.S. patent 5,139,878, discloses a fluoropolymer film structure using an adhesive tie layer of modified polyolefins. U.S. patent 6,451,925 teaches a laminate of a fluoropolymer layer and a non-fluoropolymer layer using an adhesive tie layer which is a blend of an aliphatic

polyamide and a fluorine-containing graft polymer. Additionally, U.S. patent 5,855,977 teaches applying an aliphatic di- or polyamine to one or more surfaces of a fluoropolymer or non-fluoropolymer material layer.

5 As an alternative to an adhesive tie layer, a surface treatment of one or both of the layers has been used to increase the adhesive bond strength between the two dissimilar layers. For example, U.S. patent 6,197,393 describes treating a non-fluoropolymer layer by providing a bonding composition which comprises a primary or secondary di- or polyamine and a non-fluorinated base polymer, and
10 then reacting these components to form an amine-functionalized base polymer, which base polymer materials may include polyamides, polyamide imides, polyether imides, polyimides, polyureas, polyurethanes, polyesters, polycarbonates, functionalized polyolefins and polyketones. This is then compounded with a second different non-fluorinated polymer to form a blend
15 layer. The blend layer may then be processed with a fluoropolymer layer to form multilayered articles or structures. Additionally, U.S. patent 6,096,428 teaches the step of blending a carboxyl, carboxylate, anhydride, amide, imide, hydroxyl, or oxycarbonyl functional polyolefin with an organic or inorganic base and an organo-onium compound, forming a non-fluorinated polymeric material. This
20 non-fluorinated material is then capable of being laminated to a fluoropolymer layer under heat and pressure, and formed into articles or structures. U.S. patent 5,855,977 teaches a multilayered structure having a fluoropolymer layer and a non-fluorinated polymeric layer that has an aliphatic di- or polyamine present.

25 There is a continuing need in the art for further improvements in molded articles formed from fluoropolymers. Particularly desirable are lightweight, non-breakable structures with good clarity, a high moisture barrier, good chemical resistance and low water vapor and gas transmission. More particularly, there is a

need in the art for articles formed from fluoropolymers, which articles have good properties that are acceptable for storing moisture sensitive products. Such properties include providing chemical resistance, improved product shelf life and eliminating the breakage concerns of glass containers. The present invention satisfies this need in the art. The invention provides shaped articles for storing products which articles are formed in a fluoropolymer-containing multilayer structure that exhibits excellent bond strength between a fluoropolymer layer and a thermoplastic polymer layer.

SUMMARY OF THE INVENTION

The invention provides a shaped article for storing a product, said shaped article being formed from a multilayered structure which comprises in sequence:

- a) an inner fluoropolymer layer having first and second surfaces;
- b) an adhesive tie layer, having first and second surfaces, on the inner fluoropolymer layer with the first surface of the adhesive tie layer on the first surface of the fluoropolymer layer; which adhesive tie layer comprises a combination of at least one tackifier, at least one ethylene/alpha-olefin copolymer and optionally at least one styrenic block copolymer; and
- c) an outer thermoplastic polymer layer, having first and second surfaces, on the adhesive tie layer with the first surface of the thermoplastic polymer layer on the second surface of the adhesive tie layer.

The invention also provides a shaped article for storing a product, said shaped article being formed from a multilayered structure which comprises in sequence:

- a) an inner poly(chlorotrifluoroethylene) layer having first and second surfaces;
- b) an adhesive tie layer, having first and second surfaces, on the inner poly(chlorotrifluoroethylene) layer with the first surface of the adhesive tie layer

on the first surface of the poly(chlorotrifluoroethylene) layer; which adhesive tie layer comprises a combination of at least one tackifier, at least one ethylene/alpha-olefin copolymer and optionally at least one styrenic block copolymer;

- 5 c) a polyethylene layer, having first and second surfaces, on the adhesive tie layer with the first surface of the polyethylene layer on the second surface of the adhesive tie layer; and
d) at least one polymer layer on the second surface of the polyethylene layer.

10 The invention further provides a process for forming a shaped article for storing a product which comprises:

I) forming a multilayered structure by a process which comprises:

- 15 a) forming an inner fluoropolymer layer having first and second surfaces;
b) attaching an adhesive tie layer, having first and second surfaces, to the fluoropolymer layer with the first surface of the adhesive tie layer on the first surface of the fluoropolymer layer; which adhesive tie layer comprises a combination of at least one tackifier, at least one ethylene/alpha-olefin copolymer and optionally at least one styrenic block copolymer;
20 c) attaching an outer thermoplastic polymer layer, having first and second surfaces, to the adhesive tie layer with the first surface of the thermoplastic polymer layer on the second surface of the adhesive tie layer; and

25 II) forming said multilayered structure into an article by injection molding, blow molding, co-injection blow molding, co-injection stretch-blow molding or co-extrusion blow molding techniques.

The invention still further provides a shaped article for storing a product, said shaped article being formed from a multilayered structure which comprises in sequence:

- a) a first outer thermoplastic polymer layer, having first and second surfaces;
- 5 b) a first adhesive tie layer, having first and second surfaces, on the first outer thermoplastic layer with the first surface of the first adhesive tie layer on the first surface of the first outer thermoplastic polymer layer; which first adhesive tie layer comprises a combination of at least one tackifier, at least one ethylene/alpha-olefin copolymer and optionally at least one styrenic block
- 10 copolymer; and
- c) a central fluoropolymer layer having first and second surfaces, on the first adhesive tie layer with the first surface of the central fluoropolymer layer on the second surface of the first adhesive tie layer;
- d) a second adhesive tie layer, having first and second surfaces, on the central
- 15 fluoropolymer layer with the first surface of the second adhesive tie layer on the first surface of the central fluoropolymer layer; which second adhesive tie layer comprises a combination of at least one tackifier, at least one ethylene/alpha-olefin copolymer and optionally at least one styrenic block copolymer; and
- e) a second outer thermoplastic polymer layer, having first and second surfaces,
- 20 on the second adhesive tie layer with the first surface of the second outer thermoplastic polymer layer on the second surface of the second adhesive tie layer.

The invention also provides a shaped article for storing a product, said shaped article being formed from a multilayered structure which comprises in sequence:

- a) a first outer polyethylene layer, having first and second surfaces;
- 25 b) a first adhesive tie layer, having first and second surfaces, on the first outer polyethylene layer with the first surface of the first adhesive tie layer on the first

surface of the first outer polyethylene layer; which first adhesive tie layer comprises a combination of at least one tackifier, at least one ethylene/alpha-olefin copolymer and optionally at least one styrenic block copolymer; and
c) a central poly(chlorotrifluoroethylene) layer having first and second surfaces,
5 on the first adhesive tie layer with the first surface of the central poly(chlorotrifluoroethylene) layer on the second surface of the first adhesive tie layer;
d) a second adhesive tie layer, having first and second surfaces, on the central poly(chlorotrifluoroethylene) layer with the first surface of the second adhesive
10 tie layer on the first surface of the central poly(chlorotrifluoroethylene) layer;
which second adhesive tie layer comprises a combination of at least one tackifier, at least one ethylene/alpha-olefin copolymer and optionally at least one styrenic block copolymer; and
e) a second outer polyethylene layer, having first and second surfaces, on the
15 second adhesive tie layer with the first surface of the second outer polyethylene layer on the second surface of the second adhesive tie layer.

The invention further provides a process for forming a shaped article for storing a product which comprises:

- 20 I) forming a multilayered structure by a process which comprises:
- a) forming a first outer thermoplastic polymer layer, having first and second surfaces;
 - b) attaching a first adhesive tie layer, having first and second surfaces, to the first outer thermoplastic layer with the first surface of the first adhesive
25 tie layer on the first surface of the first outer thermoplastic polymer layer;
which first adhesive tie layer comprises a combination of at least one tackifier, at least one ethylene/alpha-olefin copolymer and optionally at least one styrenic block copolymer; and

c) attaching a central fluoropolymer layer having first and second surfaces,
to the first adhesive tie layer with the first surface of the central

fluoropolymer layer on the second surface of the first adhesive tie layer;

d) attaching a second adhesive tie layer, having first and second surfaces,

to the central fluoropolymer layer with the first surface of the second

adhesive tie layer on the first surface of the central fluoropolymer layer;

which second adhesive tie layer comprises a combination of at least one
tackifier, at least one ethylene/alpha-olefin copolymer and optionally at
least one styrenic block copolymer; and

e) attaching a second outer thermoplastic polymer layer, having first and
second surfaces, to the second adhesive tie layer with the first surface of
the second outer thermoplastic polymer layer on the second surface of the
second adhesive tie layer; and

II) forming said multilayered structure into an article by injection molding, co-
injection blow molding, co-injection stretch-blow molding or co-extrusion blow
molding techniques.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional side-view of a shaped article of the invention which
contains a liquid product.

Fig. 2 is a cross-sectional side-view of a shaped article of the invention that
contains a solid product which product is adjacent to an inner fluoropolymer
layer.

Fig. 3 is a plan-view, schematic representation of a multilayered structure of the invention having an inner fluoropolymer layer attached to an outer thermoplastic polymer layer via an adhesive tie layer of the invention and further having a polymer layer attached to the outer thermoplastic polymer layer via another adhesive tie layer.

Fig. 4 is a plan-view, schematic representation of a multilayered structure of the invention having multiple additional polymeric layers attached to said outer thermoplastic polymer layer.

Fig. 5 is a plan-view, schematic representation of a multilayered structure of the invention having a central fluoropolymer layer, an adhesive tie layer on either side of the central fluoropolymer layer and a plurality of polymer layers attached to the outer thermoplastic polymer layer via additional adhesive layers.

Fig. 6 is a cross sectional side-view of a shaped article of the invention that contains a liquid-product with the shaped article being formed from a multilayered structure having a central fluoropolymer layer, an adhesive tie layer on either side of the central fluoropolymer layer and an outer thermoplastic polymer layer on each adhesive tie layer.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As can be seen in Fig. 1, Fig. 2 and Fig. 6, the invention provides shaped articles suitable for storing a product 20, which articles are formed from a multilayered structure such as those shown in Fig. 3 through Fig. 5. In one embodiment of the invention, the multilayered structure of the invention includes an inner

fluoropolymer layer 12 attached to an outer thermoplastic polymer layer 14. These layers are attached by an intermediate adhesive tie layer 16 which is a combination of at least one tackifier, at least one ethylene/alpha-olefin copolymer and optionally one or more styrenic block copolymers. This adhesive tie layer 16 imparts excellent bond strength between adjacent layers of the structure and particularly between the fluoropolymer layer 12 and the outer thermoplastic polymer layer 14. Shaped articles, such as those illustrated in Fig. 1 and Fig. 2, are preferably formed from this multilayered structure such that the fluoropolymer layer 12 is the innermost layer of the article and is positioned adjacent to a product placed inside the shaped article 10.

In an alternate embodiment of the invention, a second outer thermoplastic polymer layer 14 is attached to another surface of said fluoropolymer layer 12 via a second intermediate adhesive tie layer 16 such that the fluoropolymer layer is the central layer of the multilayered structure, being positioned between the two thermoplastic polymer layers 14 and adhesive tie layers 16. This embodiment is illustrated in Fig. 5. Fig. 6 illustrates a shaped article formed from this type of multilayered structure.

With regard to the individual layers of the shaped articles 10 of the invention, the inner or the central fluoropolymer layer 12 has first and second surfaces and is joined with an adhesive tie layer 16 such that the first surface of the inner fluoropolymer layer 12 is in contact with a first surface of the adhesive tie layer 16. Fluoropolymer materials are commonly known for their excellent chemical resistance and excellent release properties, as well as their moisture and vapor barrier properties. Accordingly, fluoropolymer materials are desirable components for packaging applications. In the preferred embodiment of the invention, the fluoropolymer layer 12 may be comprised of fluoropolymer

homopolymers or copolymers or blends thereof as are well known in the art and are described in, for example, U.S. patent numbers 4,510,301, 4,544,721 and 5,139,878. Preferred fluoropolymers include, but are not limited to, homopolymers and copolymers of chlorotrifluoroethylene, ethylene-
5 chlorotrifluoroethylene copolymer, ethylene-tetrafluoroethylene copolymer, fluorinated ethylene-propylene copolymer, perfluoroalkoxyethylene, polychlorotrifluoroethylene, polytetrafluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, and copolymers and blends thereof. As used herein, copolymers include polymers having two or more monomer components. The
10 most preferred fluoropolymers include homopolymers and copolymers of poly(chlorotrifluoroethylene). Particularly preferred are PCTFE (polychlorotrifluoroethylene homopolymer) materials sold under the ACLONTM trademark and which are commercially available from Honeywell International Inc. of Morristown, New Jersey.

15 In the production of the shaped articles 10 of the invention, outer thermoplastic polymer layer 14 has first and second surfaces and is attached to the fluoropolymer layer 12 such that the first surface of the outer thermoplastic polymer layer 14 is in contact with the second surface of the adhesive tie layer 16.
20 Suitable thermoplastic polymer materials include non-fluoropolymer materials such as linear or branched polyolefin homopolymers, linear or branched polyolefin copolymers, cyclic olefin homopolymers, copolymers of cyclic olefins and linear or branched polyolefin homopolymers, copolymers of cyclic olefins and linear or branched polyolefin copolymers, ethylene vinyl acetate copolymers,
25 polyesters such as polyethylene terephthalate, polyamides, polyvinyl chloride, polyvinylidene chloride, polystyrene, styrenic copolymers, polyisoprene, polyurethanes, ethylene ethyl acrylate, ethylene acrylic acid copolymers and combinations thereof. The thermoplastic polymer layer 14 may also comprise

another fluoropolymer layer. In the preferred embodiment of the invention, outer thermoplastic polymer layer 14 comprises polyethylene.

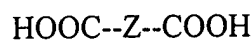
Suitable polyolefins for use herein include polymers of alpha-olefin monomers having from about 3 to about 20 carbon atoms and include homopolymers, copolymers (including graft copolymers), and terpolymers of alpha-olefins. Illustrative homopolymer examples include polyethylenes such as low density polyethylene (LDPE), ultra low density polyethylene (ULDPE), linear low density polyethylene (LLDPE), metallocene linear low density polyethylene (m-LLDPE), medium density polyethylene (MDPE), and high density polyethylene (HDPE). Also preferred are polypropylene, polybutylene, polybutene-1, poly-3-methylbutene-1, poly-pentene-1, poly-4,4 dimethylpentene-1, poly-3-methylpentene-1, polyisobutylene, poly-4-methylhexene-1, poly-5-ethylhexene-1, poly-6-methylheptene-1, polyhexene-1, polyoctene-1, polynonene-1, polydecene-1, polydodecene-1 and the like. Also suitable are blends of these polyolefins.

Polyolefins such as polyethylenes are commonly differentiated based on the density which results from their numbers of chain branches per 1,000 carbon atoms in the polyethylene main chain in the molecular structure. Branches typically are C₃-C₈ olefins, more preferably propylene, butene, hexene or octene. For example, HDPE has very low numbers of short chain branches (less than 20 per 1,000 carbon atoms), resulting in a relatively high density, i.e. density ranges from about 0.94 gm/cc to about 0.97 gm/cc. LLDPE has more short chain branches, in the range of 20 to 60 per 1,000 carbon atoms with a density of about 0.90 to about 0.93 gm/cc. LDPE with a density of about 0.91 to about 0.93 gm/cc has long chain branches (20-40 per 1,000 carbon atoms) instead of short chain branches in LLDPE and HDPE. ULDPE has a higher concentration of short chain branches than LLDPE and HDPE, i.e. in the range of about 80 to about 250 per

1,000 carbon atoms and has a density of from about 0.88 to about 0.92 gm/cc.

Illustrative copolymers and terpolymers include copolymers and terpolymers of alpha-olefins with other olefins such as ethylene-propylene copolymers; ethylene-butene copolymers; ethylene-pentene copolymers; ethylene-hexene copolymers; and ethylene-propylene-diene copolymers (EPDM). The term polyolefin as used herein also includes acrylonitrilebutadiene-styrene (ABS) polymers, copolymers with vinyl acetate, acrylates and methacrylates and the like. Preferred polyolefins are those prepared from alpha-olefins, most preferably ethylene polymers, copolymers, and terpolymers. The above polyolefins may be obtained by any known process. The polyolefin may have a weight average molecular weight of about 1,000 to about 1,000,000, and preferably about 10,000 to about 500,000 as measured by high performance liquid chromatography (HPLC). Preferred polyolefins are polyethylene, polypropylene, polybutylene and copolymers, and blends thereof. The most preferred polyolefin is polyethylene. The most preferred polyethylenes are low density polyethylenes.

Suitable polyamides within the scope of the invention non-exclusively include homopolymers or copolymers selected from aliphatic polyamides and aliphatic/aromatic polyamides having a weight average molecular weight of from about 10,000 to about 100,000. General procedures useful for the preparation of polyamides are well known to the art. Such include the reaction products of diacids with diamines. Useful diacids for making polyamides include dicarboxylic acids which are represented by the general formula



wherein Z is representative of a divalent aliphatic radical containing at least 2 carbon atoms, such as adipic acid, sebacic acid, octadecanedioic acid, pimelic

acid, suberic acid, azelaic acid, dodecanedioic acid, and glutaric acid. The dicarboxylic acids may be aliphatic acids, or aromatic acids such as isophthalic acid and terephthalic acid. Suitable diamines for making polyamides include those having the formula

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wherein n has an integer value of 1-16, and includes such compounds as trimethylenediamine, tetramethylenediamine, pentamethylenediamine, 10 hexamethylenediamine, octamethylenediamine, decamethylenediamine, dodecamethylenediamine, hexadecamethylenediamine, aromatic diamines such as p-phenylenediamine, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulphone, 4,4'-diaminodiphenylmethane, alkylated diamines such as 2,2-dimethylpentamethylenediamine, 2,2,4-trimethylhexamethylenediamine, and 15 2,4,4 trimethylpentamethylenediamine, as well as cycloaliphatic diamines, such as diaminodicyclohexylmethane, and other compounds. Other useful diamines include heptamethylenediamine, nonamethylenediamine, and the like.

Useful polyamide homopolymers include poly(4-aminobutyric acid) (nylon 4), 20 poly(6-aminohexanoic acid) (nylon 6, also known as poly(caprolactam)), poly(7-aminohexanoic acid) (nylon 7), poly(8-aminooctanoic acid)(nylon 8), poly(9-aminononanoic acid) (nylon 9), poly(10-aminodecanoic acid) (nylon 10), poly(11-aminoundecanoic acid) (nylon 11) and poly(12-aminododecanoic acid) (nylon 12), while useful copolymers include nylon 4,6, poly(hexamethylene adipamide) 25 (nylon 6,6), poly(hexamethylene sebacamide) (nylon 6,10), poly(heptamethylene pimelamide) (nylon 7,7), poly(octamethylene suberamide) (nylon 8,8), poly(hexamethylene azelamide) (nylon 6,9), poly(nonamethylene azelamide) (nylon 9,9), poly(decamethylene azelamide) (nylon 10,9),

poly(tetramethylenediamine-co-oxalic acid) (nylon 4,2), the polyamide of n-dodecanedioic acid and hexamethylenediamine (nylon 6,12), the polyamide of dodecamethylenediamine and n-dodecanedioic acid (nylon 12,12) and the like. Other useful aliphatic polyamide copolymers include caprolactam/hexamethylene adipamide copolymer (nylon 6,6/6), hexamethylene adipamide/caprolactam copolymer (nylon 6/6,6), trimethylene adipamide/hexamethylene azelaamide copolymer (nylon trimethyl 6,2/6,2), hexamethylene adipamide-hexamethylene-azelaamide caprolactam copolymer (nylon 6,6/6,9/6) and the like. Also included are other nylons which are not particularly delineated here.

Of these polyamides, preferred polyamides include nylon 6, nylon 6,6, nylon 6/6,6 as well as mixtures of the same. Of these, nylon 6 is most preferred.

Aliphatic polyamides used in the practice of this invention may be obtained from commercial sources or prepared in accordance with known preparatory techniques. For example, poly(caprolactam) can be obtained from Honeywell International Inc., Morristown, New Jersey.

Exemplary of aliphatic/aromatic polyamides include poly(tetramethylenediamine-co-isophthalic acid) (nylon 4,I), polyhexamethylene isophthalamide (nylon 6,I), hexamethylene adipamide/hexamethylene-isophthalamide (nylon 6,6/6I), hexamethylene adipamide/hexamethyleneterephthalamide (nylon 6,6/6T), poly(2,2,2-trimethyl hexamethylene terephthalamide), poly(m-xylylene adipamide) (MXD6), poly(p-xylylene adipamide), poly(hexamethylene terephthalamide), poly(dodecamethylene terephthalamide), polyamide 6T/6I, polyamide 6/MXDT/I, polyamide MXDI, and the like. Blends of two or more aliphatic/aromatic polyamides can also be used. Aliphatic/aromatic polyamides can be prepared by known preparative techniques or can be obtained from commercial sources.

Other suitable polyamides are described in U.S. patents 4,826,955 and 5,541,267, which are incorporated herein by reference.

Suitable cyclic (cyclo) olefin polymers (homopolymers, copolymers or blends) are described, for example, in U.S. patents 5,218,049; 5,783,273 and 5,912,070, which are incorporated herein by reference. U.S. patent 5,218,049 discloses films composed of cyclic olefins. U.S. patent 5,783,273 discloses press-through blister packaging materials comprising a sheet of a cyclic olefin copolymer. U.S. patent 5,912,070 discloses a packaging material comprising a layer of a cyclic olefin, a layer of a polyester and an intermediate adhesive. In the most preferred embodiment of the invention, the thermoplastic polymer layer 14 comprises a cyclic olefin copolymer. Cyclic olefins may be obtained commercially from Mitsui Petrochemical Industries, Ltd. of Tokyo, Japan, or Ticona of Summit, New Jersey.

The use of a cyclic olefin copolymer (COC) is advantageous because of its attractive properties. Cyclic olefin copolymers are amorphous, clear, random copolymers. They combine excellent optical and electrical properties with low density and moisture absorption, with high stiffness and strength. Some of the beneficial properties of COC's include a high moisture barrier, low moisture absorption, high light transmission, low birefringence, high stiffness and strength. In addition, COC's exhibit good heat sealability and excellent heat resistance properties, dimensional stability, easy metallizability, ready processability in conventional injection molding, film extrusion, blow molding and thermoforming techniques, and good compatibility with other non-fluorinated polymers.

The adhesive tie layer 16 preferably comprises a combination of at least one tackifier and at least one ethylene/alpha-olefin copolymer. Combinations of said

adhesive components include blends of said components. As used herein, a tackifier is intended to describe a material that improves the tackiness or stickiness of an adhesive without the formation of chemical bonds. Preferred tackifiers or tackifier blends preferably have an interlayer bond strength of at least about 45 g/cm, as determined by the ASTM F904 method. Suitable tackifiers non-exclusively include terpene-based polymers, coumarone-based polymers, phenol-based polymers, rosin-based polymers, rosin esters and hydrogenated rosin esters, petroleum and hydrogenated petroleum-based polymers, styrene-based polymers and mixtures thereof.

Suitable terpene-based polymers include terpene polymers of alpha-pinene, beta-pinene, dipentel, limonene, myrcene, bornylene and camphene, and phenol-modified terpene-based polymers obtained by modifying these terpene-based polymers with phenols.

Suitable coumarone-based polymers include, for example, coumarone-indene polymers and phenol-modified coumarone-indene polymers.

Suitable phenol-based polymers include reaction products of phenols such as phenol, cresol, xylenol, resorcinol, p-tert-butylphenol, and p-phenylphenol with aldehydes such as formaldehyde, acetaldehyde and furfural, and rosin-modified phenol polymers.

Suitable rosin-based polymers include unmodified rosin (e.g., wood, gum, or tall oil) and rosin derivatives. Rosin-based polymers can be classified by their rosin acids, which are either an abietic acid or a pimaric acid. Abietic acid-type rosins are preferred. Rosin derivatives include polymerized rosin, disproportionated rosin, hydrogenated rosin, and esterified rosin. Representative examples of such

rosin derivatives include pentaerythritol esters of tall oil, gum rosin, wood rosin, or mixtures thereof.

Suitable petroleum and hydrogenated petroleum-based polymers include aliphatic petroleum polymers, alicyclic petroleum polymers, aromatic petroleum polymers using styrene, alpha-methylstyrene, vinyltoluene, indene, methylindene, butadiene, isoprene, piperylene and pentylene as raw materials, and homopolymers or copolymers of cyclopentadiene. Preferable petroleum polymers include aliphatic hydrocarbon polymers and hydrogenated polycyclodienic polymers. A wide range of unsaturated cyclic monomers can be obtained from petroleum derivatives, such as, for example, cyclopentene derivatives, cyclopentadiene derivatives, cyclohexene derivatives, cyclohexadiene derivatives, and the like. A wide range of unsaturated monomers can be obtained from petroleum derivatives, such as, for example, ethylene derivatives, propylene derivatives, butadiene derivatives, isoprene derivatives, pentenes, hexenes, heptenes, and the like.

Suitable styrene-based polymers include homopolymers which are low molecular weight polymers comprising styrene as a principal component, and copolymers of styrene with, for example, alpha-methylstyrene, vinyltoluene, and butadiene rubber.

The most preferred tackifiers are terpene-based polymers, petroleum and hydrogenated petroleum-based polymers.

In the preferred embodiment of the invention, the tackifier preferably comprises from greater than about 1% by weight to about 60% by weight of said tackifier-ethylene/alpha-olefin copolymer combination, more preferably from about 5% by

weight to about 30% by weight, and most preferably from about 15% by weight to about 25% by weight. Accordingly, said ethylene/alpha-olefin copolymer preferably comprises from about 40% by weight to about 99% by weight of said tackifier-ethylene/alpha-olefin copolymer combination, more preferably from
5 about 70% by weight to about 95% by weight and most preferably from about 75% by weight to about 85% by weight.

The ethylene/alpha-olefin copolymers of the adhesive composition are generally characterized as plastomers. In general, plastomers are comprised of
10 polymerized, random copolymers of ethylene and one or more olefin comonomers.

Suitable ethylenes which may comprise the ethylene component of the ethylene/alpha-olefin copolymer preferably include polyethylenes such as low
15 density polyethylene, ultra low density polyethylene, linear low density polyethylene, metallocene linear low density polyethylene, medium density polyethylene or high density polyethylene. Preferred ethylenes include polyethylene graft copolymers and linear and low density polyethylene copolymers.

20 Suitable olefins which may be copolymerized with an ethylene to form the ethylene/alpha-olefin copolymer include linear and branched alpha-olefins having 3 to 20 carbon atoms of which preparations are described, for example, in U.S. patents 3,645,992, 5,272,236, 5,278,272 and 6,319,979. Specific examples of the
25 linear alpha-olefins are propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridocene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nanodecene and 1-eicocene. Specific examples of the branched alpha-olefins are 3-methyl-1-butene,

3-methyl-1-pentene, 4-methyl-1-pentene, 2-ethyl-1-hexene and 2,2,4-trimethyl-1-pentene. Of these, linear propylene, 1-butene, 1-pentene, 1-hexene, 1-octene and 1-decene are preferred. These alpha-olefins may be used singularly or in combination.

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In the preferred embodiment of the invention, the ethylene/alpha-olefin copolymer comprises a copolymer comprising an ethylene and at least one alpha-olefin having from three to twenty carbon atoms (C_3 - C_{20}). For example, the ethylene/alpha-olefin copolymer may comprise a copolymer of a linear low
10 density polyethylene and a C_3 - C_{20} alpha-olefin, a terpolymer comprising ethylene and more than one C_3 - C_{20} alpha-olefin or a polyethylene graft copolymer including at least one C_3 - C_{20} alpha-olefin.

In accordance with the present invention, suitable ethylene/alpha-olefin
15 copolymers include modified compositions having at least one functional moiety selected from the group consisting of unsaturated polycarboxylic acids and anhydrides thereof. Such unsaturated carboxylic acid and anhydrides include maleic acid and anhydride, fumaric acid and anhydride, crotonic acid and anhydride, citraconic acid and anhydride, itaconic acid and anhydride and the like.
20 Of these, the most preferred is maleic anhydride. In accordance with the invention, modified ethylene/alpha-olefin copolymer compositions preferably comprise from about 0.001 to about 20 percent by weight of the functional moiety, based on the total weight of the modified plastomer. More preferably the functional moiety comprises from about 0.05 to about 10 percent by weight, and
25 most preferably from about 0.1 to about 5 percent by weight of the functional moiety. In the preferred embodiment of the invention, the ethylene/alpha-olefin copolymer is unmodified. However, a modified ethylene/alpha-olefin copolymer

is preferred when said thermoplastic polymer layer comprises a polar material such as nylon or polyester.

5 In the preferred embodiment of the invention, the ethylene/alpha-olefin copolymers preferably have an ethylene content of from about 35 mole % to about 99.5 mole %, more preferably from about 70 mole % to about 90 mole % and most preferably from about 75 mole % to about 85 mole %. Accordingly, the ethylene/alpha-olefin copolymers of the invention preferably have an alpha-olefin content of from about 0.5 mole % to about 65 mole %, more preferably from
10 about 10 mole % to about 30 mole % and most preferably from about 15 mole % to about 25 mole %.

The adhesive tie layer 16 may further include at least one styrenic block copolymer. The styrenic block copolymer is preferably a styrenic copolymer
15 selected from the group consisting of a styrene/ethylene-propylene/styrene block copolymer (SEPS), a styrene/ethylene ethylene-propylene random/styrene block copolymer (SEEPS), a styrene/butadiene/styrene block copolymer (SBS), a styrene/ethylene butylene random/styrene block copolymer (SEBS), a styrene/isobutylene/styrene block copolymer (SIBS), a styrene/isoprene/styrene
20 block copolymer (SIS), a styrene/hydrogenated butylene/styrene block copolymer (SHBS) and a maleic anhydride grafted styrene/ethylene butylene/styrene copolymer (MAH-g-SEBS). Styrenic block copolymers are available in either a diblock type or the more common triblock types and mixtures thereof. If
25 included, said styrenic block copolymer preferably comprises from about 0.1% by weight to about 80% by weight of said adhesive combination, more preferably from about 0.5% by weight to about 15% by weight and most preferably from about 1% by weight to about 6% by weight. The preferred styrenic block copolymers are styrene/isoprene/styrene block copolymer and styrene/ethylene

butylene random/styrene block copolymer. Of these, styrene/isoprene/styrene block copolymer is the most preferred.

As illustrated in Fig. 3 and Fig. 4, the multilayered structures which are formed into the shaped articles 10 described herein may further comprise at least one additional polymer layer 18 that may be attached on the outer surface of the outer thermoplastic polymer layer 14. Said at least one additional polymer layer 18 may comprise a layer of any material described herein, but is by no means limited to such materials. For example, optional layer or layers 18 may comprise a layer of a fluoropolymer, a polyamide, a polyolefin, an ethylene vinyl acetate copolymer, polyethylene terephthalate, polyvinyl chloride, polyvinylidene chloride, polystyrene, styrenic copolymers, polyisoprene, polyurethanes, an ethylene acrylic acid polymer, a cyclic olefin homopolymer or copolymer and combinations thereof. As seen in Fig. 4, the multilayered structure may include a plurality of additional layers 18. Said at least one additional layer 18 is preferably, but not necessarily, attached to the other layers of the structure via another adhesive tie layer 16 formed from said adhesive combination.

Each of the inner or the central fluoropolymer layer 12, adhesive tie layer 16, outer thermoplastic polymer layer 14 and any additional layers may optionally also include one or more conventional additives whose uses are well known to those skilled in the art. The use of such additives may be desirable in enhancing the processing of the compositions as well as improving the products or articles formed therefrom. Examples of such include: oxidative and thermal stabilizers, lubricants, release agents, flame-retarding agents, oxidation inhibitors, oxidation scavengers, dyes, pigments and other coloring agents, ultraviolet light absorbers and stabilizers, organic or inorganic fillers including particulate and fibrous fillers, reinforcing agents, nucleators, plasticizers, as well as other conventional

additives known to the art. Such may be used in amounts, for example, of up to about 30 % by weight of the overall layer composition. It is also preferred that no layer of the structure contains a tackifier composition but for layers that are labeled as adhesive tie layers. It is particularly preferred that neither of the
5 outermost layers of the structures described herein contain a tackifier composition as defined herein. Representative ultraviolet light stabilizers include various substituted resorcinols, salicylates, benzotriazoles, benzophenones, and the like. Suitable lubricants and release agents include wax, stearic acid, stearyl alcohol, and stearamides. Exemplary flame-retardants include organic halogenated
10 compounds, including decabromodiphenyl ether and the like as well as inorganic compounds. Suitable coloring agents including dyes and pigments include cadmium sulfide, cadmium selenide, titanium dioxide, phthalocyanines, ultramarine blue, nigrosine, carbon black and the like. Representative oxidative and thermal stabilizers include the Period Table of Element's Group I metal
15 halides, such as sodium halides, potassium halides, lithium halides; as well as cuprous halides; and further, chlorides, bromides, iodides. Also acceptable are hindered phenols, hydroquinones, aromatic amines as well as substituted members of those above mentioned groups and combinations thereof. Exemplary plasticizers include lactams such as caprolactam and lauryl lactam, sulfonamides
20 such as o,p-toluenesulfonamide and N-ethyl, N-butyl benylenesulfonamide, and combinations of any of the above, as well as other plasticizers known to the art.

The multilayered structures of the invention are formed into shaped articles 10
suitable for storing a product 20. The shaped articles 10 of the invention may be
25 produced by conventional methods known in the art, including well known injection molding, co-injection blow molding, co-injection stretch-blow molding or co-extrusion blow molding techniques and by forming the structure around a suitable mold and heating in a method well known in the art.

The most preferred method for producing the shaped articles 10 of the invention is co-extrusion blow molding. Co-extrusion blow molding is a process in which individual extruders feed the individual components into a co-extrusion head, where a multi-layer parison is formed and extruded. The parison, still in its melt form, is then sandwiched between two mold halves. Once the mold halves have fully closed on the parison, air is introduced into the center of the parison which in turn expands the parison into the configuration of the mold cavity. The material then solidifies due to lower temperatures introduced from the surface of the chilled mold halves. The mold halves are then opened up and the newly formed container is ejected from the mold.

Alternately, the shaped articles 10 may be formed by first combining the individual layers described herein to form a multilayered film, followed by subsequently shaping the multilayered film into a desired shaped article 10. In this embodiment, multilayered films may be produced by conventional methods useful in producing multilayer films, including coextrusion and lamination techniques. In a conventional coextrusion process, the polymeric material for the individual layers are fed into infeed hoppers of a like number of extruders, each extruder handling the material for one or more of the layers. The melted and plasticated streams from the individual extruders are directly fed to a multi-manifold die and then juxtaposed and combined into a layered structure or combined into a layered structure in a combining block and then fed into a single manifold or multi-manifold co-extrusion die. The layers emerge from the die as a single multiple layer film of polymeric material. After exiting the die, the film is cast onto a first controlled temperature casting roll, passes around the first roll, and then onto a second controlled temperature roll. The controlled temperature rolls largely control the rate of cooling of the film after it exits the die. Additional

rolls may be employed. In another method, the film forming apparatus may be one which is referred to in the art as a blown film apparatus and includes a multi-manifold circular die head for bubble blown film through which the plasticized film composition is forced and formed into a film bubble which may ultimately be collapsed and formed into a film. Typical coextrusion techniques are described in U.S. patents 5,139,878 and 4,677,017. One advantage of coextruded films is the formation of a multilayer film in a one process step by combining molten layers of each of the film layers, as well as any other optional film layers, into a unitary film structure.

Alternately, the individual layers may first be formed as separate layers and then laminated together under heat and pressure with or without intermediate adhesive layers. Lamination techniques are well known in the art. Typically, laminating is done by positioning the individual layers on one another under conditions of sufficient heat and pressure to cause the layers to combine into a unitary film.

Typically the fluoropolymer layer, the thermoplastic polymer layer, the adhesive and any additional layers are positioned on one another, and the combination is passed through the nip of a pair of heated laminating rollers by techniques well known in the art. Lamination heating may be done at temperatures ranging from about 120 ° C. to about 175 ° C., preferably from about 150 ° C. to about 175 ° C., at pressures ranging from about 5 psig (0.034 MPa) to about 100 psig (0.69 MPa), for from about 5 seconds to about 5 minutes, preferably from about 30 seconds to about 1 minute. In the preferred embodiment of the invention, the shaped articles 10 are formed by co-extrusion blow molding.

In the embodiment where the multilayered structure of the invention is formed into a film prior to being molded into a shaped article 10, the film may be uniaxially or biaxially oriented prior to molding. The layers may be drawn to a

draw ratio of from 1.5:1 to 5:1 uniaxially in at least one direction, i.e. its longitudinal direction, its transverse direction or biaxially in each of its longitudinal and transverse directions. For the purposes of the present invention the term draw ratio is an indication of the increase in the dimension in the direction of draw. For example, the multilayered structure may be uniaxially oriented from about 1.3 to about 10 times in either its longitudinal or transverse directions, or the multilayered structure may be biaxially oriented from about 1.5 to about 5 times each of its longitudinal and transverse directions. The structure may also be drawn to a lesser or greater degree in either or both of said longitudinal and transverse directions. The layers may be simultaneously biaxially oriented, for example orienting a film in both the machine and transverse directions at the same. This results in dramatic improvements in clarity, strength and toughness properties, as well as an improved moisture vapor transmission rate.

Although each layer of the multilayer structures may have a different thickness, the fluoropolymer layer 12 has a preferred thickness of from about 0.01 mil (0.25 μm) to about 20 mil (508 μm), more preferably from about 0.1 mil (2.5 μm) to about 10 mil (254 μm), and most preferably from about 0.3 mil (7.6 μm) to about 6 mil (152 μm). The thermoplastic polymer layer 14 has a thickness of about 0.04 mil (1 μm) to about 200 mil (5080 μm), a preferred thickness of from about 2 mil (50 μm) to about 100 mil (2540 μm), more preferably from about 5 mil (127 μm) to about 60 mil (1520 μm). The adhesive tie layers have a preferred thickness of from about 0.04 mil (1 μm) to about 20 mil (508 μm), more preferably from about 0.3 mil (7.6 μm) to about 10 mil (254 μm). Additional layers preferably have a thickness of from about 0.04 mil (1 μm) to about 200 mil (5080 μm), more preferably from about 0.4 mil (10 μm) to about 100 mil (2540 μm) and most

preferably from about 0.8 mil (20 μm) to about 60 mil (1520 μm). While such thicknesses are referenced, it is to be understood that other layer thicknesses may be produced to satisfy a particular need and yet fall within the scope of the present invention.

5

The moisture vapor transmission rate (MVTR) of such structures of the invention may be determined via the procedure set forth in ASTM F1249. In the preferred embodiment, the structures of the invention have a preferred MVTR of from about 1.0 or less $\text{g}/100 \text{ in}^2/\text{day}$ (15.5 $\text{g}/\text{m}^2/\text{day}$) of the overall structure at 37.8°C and 100% relative humidity (RH), more preferably from 0.0005 to about 0.7 $\text{g}/100 \text{ in}^2/\text{day}$ (0.0077 to about 10.7 $\text{g}/\text{m}^2/\text{day}$) of the overall structure, and most preferably from 0.001 to about 0.06 $\text{g}/100 \text{ in}^2/\text{day}$ (0.015 to about 0.93 $\text{g}/\text{m}^2/\text{day}$) of the overall structure, as determined by water vapor transmission rate measuring equipment available from, for example, Mocon.

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The oxygen transmission rate (OTR) of the structures of the invention may be determined via the procedure of ASTM D-3985 using an OX-TRAN 2/20 instrument manufactured by Mocon, operated at 25°C, 0% RH. In the preferred embodiment, the overall structure of the invention has a preferred OTR of from about 50 or less $\text{cc}/100 \text{ in}^2/\text{day}$ (775 $\text{g}/\text{m}^2/\text{day}$), more preferably from about 0.001 to about 20 $\text{cc}/100 \text{ in}^2/\text{day}$ (0.015 to about 310 $\text{g}/\text{m}^2/\text{day}$), and most preferably from about 0.001 to about 10 $\text{cc}/100 \text{ in}^2/\text{day}$ (0.015 to about 150 $\text{cc}/\text{m}^2/\text{day}$).

20

The shaped articles of the invention are useful for a variety of end applications, such as for medical packaging, pharmaceutical packaging, packaging of other moisture sensitive products and other industrial uses, particularly as bottles for packaging liquid or solid food or pharmaceutical products. As described herein,

25

two alternate embodiments of the invention are presented. As Fig. 1 and Fig. 2 illustrate, the shaped articles 10 may be formed such that the fluoropolymer layer of the multilayered structure is the innermost layer of the article and the closest layer of the structure to said product. Alternately, as illustrated in Fig. 6, the shaped articles 10 may be formed such that the fluoropolymer is a central layer of the structure, being positioned between a pair of adhesive layers 16 and a pair of outer thermoplastic polymer layers 14. Regardless of the construction, the articles or bottles formed therefrom exhibit excellent interlayer bond strength between the inner or central fluoropolymer layer and an adjacent thermoplastic polymer layer. Such articles are lightweight, non-breakable structures with good clarity, a high moisture barrier, good chemical resistance and low water vapor and gas transmission properties. Accordingly, such articles are particularly well suited for storing and increasing the shelf life of such moisture sensitive products.

The following non-limiting examples serve to illustrate the invention.

EXAMPLE 1 (COMPARATIVE)

A three-layer HDPE/PCTFE/HDPE (Unival DMDA-6220 from Dow Plastics/AclonTM 1180 from Honeywell International/Unival DMDA-6220 NT7 from Dow Plastics) bottle was prepared in a multilayer coextrusion blow-molding operation. The PCTFE (density: 2.11 g/cm³; viscosity: 82zst; DSC melting point: 211°C) and the HDPE (density: 0.953 g/cm³; melt index (ASTM D1238): 0.38g/10 minutes at 190°C and 2.16kg load; DSC melting point: 131°C) were simultaneously extruded. Six single screw extruders were involved in the operation. The dimensions of the involved extruders and a set of extrusion conditions are listed in Table 1. Molten material from Extruder 1 went into the die head and was formed into a circular downstream around the blow pin at the die head gradually gaining layers with materials in order of extruder number on

the way to the die exit. A layered circular molten parison, having a cross sectional area of 4.9cm^2 , was pumped out at the die exit into a mold and blown out to fill up a cavity of a mold of a rotary mold system which rotated at 3 rpm. A cross-sectional area of the cavity of 20.7 cm long increased gradually in the bottle neck zone of 9 cm long, changing the shape of the cross section from a circle to an oval. A cross section below the bottle neck is an oval rectangle whose minimum and maximum diagonal distances, cross sectional area, and height were 5 cm and 8.7 cm, 39cm^2 , and 11.7 cm, respectively. The temperature of the mold was constantly maintained at 10°C throughout the operation.

TABLE 1

Equipment, Material and Processing Conditions

Extruder #		EXT 1	EXT 2	EXT 3	EXT 4	EXT 5	EXT 6
Screw Specification	Diameter (mm)	50.8	31.8	38.1	31.8	50.8	50.8
	Length/Diameter Ratio	24/1	24/1	24/1	24/1	24/1	24/1
Resin		HDPE	HDPE	PCTFE	HDPE	HDPE	HDPE
Temperature ($^\circ\text{C}$)	Barrel Zone 1	191	191	232	191	191	191
	Barrel Zone 2	204	204	288	204	204	204
	Barrel Zone 3	204	204	288	204	204	204
	Elbow Connector	204	204	288	204	204	204
	Transfer Pipe	204	204	288	204	204	204
	Die Head	210	210	210	210	210	210
Screw Speed (rpm)		28	15	12	15	28	28

The resulting three layer (HDPE/PCTFE/HDPE) bottle had a gauge profile of about $254\text{ }\mu\text{m}/25\text{ }\mu\text{m}/457\text{ }\mu\text{m}$ from inside to outside when they were taken from the wider side of the fully blown oval rectangle zone below the bottle neck. The

resulting total thickness of the sample was about 736 μm . The interlayer bond strength of the resulting three-layer (HDPE/PCTFE/HDPE) bottle was determined by using a standard ASTM testing method (ASTM F904). The test was done at a constant cross head speed of 30.48 cm/min with the un-separated portion of the specimen supported at 90° to the direction of the draw. No considerable bond strength (~ 0 g/2.54 cm) was found between HDPE and PCTFE layers from anywhere of the bottle.

EXAMPLE 2

A five-layer HDPE/tie layer/PCTFE/tie layer/HDPE (Unival DMDA-6220 from Dow Plastics/ AdmerTM SF600 from Mitsui Chemicals/ AclonTM 1180 from Honeywell/ AdmerTM SF600 from Mitsui Chemical/ Unival DMDA-6220 NT7 from Dow Plastics) bottle was prepared in a multilayer coextrusion blow-molding operation. The AdmerTM SF600 (density: .088 g/cm³; melt index (ASTM D1238): 3.5g/10 minutes at 190°C and 2.16kg load; Vicat softening point (ASTM D1525): lower than 40 °C) was simultaneously extruded as a tie layer between HDPE and PCTFE layers under a set of conditions listed in Table 2. The AdmerTM SF600 is a mixture of ethylene-propylene copolymer modified with maleic anhydride and a tackifier. All the other machine settings and processing parameters not specified in Table 2 were the same as those in Example 1.

TABLE 2

Equipment, Material and Processing Conditions

Extruder #		EXT 1	EXT 2	EXT 3	EXT 4	EXT 5	EXT 6
Screw Specification	Diameter (mm)	50.8	31.8	38.1	31.8	50.8	50.8
	Length/Diameter Ratio	24/1	24/1	24/1	24/1	24/1	24/1
Resin		HDPE	tie layer	ACLON	tie layer	HDPE	HDPE
Temperature (°C)	Barrel Zone 1	191	135	232	135	191	191
	Barrel Zone 2	204	199	288	199	204	204
	Barrel Zone 3	204	232	288	232	204	204
	Elbow Connector	204	232	288	232	204	204
	Transfer Pipe	204	232	288	232	204	204
	Die Head	210	210	210	210	210	210
Screw Speed (rpm)		28	20	12	20	28	28

5 The five-layer (HDPE/tie layer/PCTFE/tie layer/HDPE) bottle showed a gauge
 profile of about 229 μm /51 μm /25 μm /51 μm /432 μm from inside to outside
 when they were taken from the wider side of the fully blown oval rectangle zone
 below the bottle neck. The resulting total thickness of the zone was about 788
 μm . Interlayer bond strength between HDPE and PCTFE layer in the five layer
 (HDPE/tie layer/PCTFE/tie layer/HDPE) bottle was determined by using a
 10 standard ASTM testing method (ASTM F904). The testing method was described
 in Example 1. The resulting interlayer bond strength between HDPE and PCTFE
 layers of the wider side of the fully blown oval rectangle zone was about
 1600g/2.54 cm.